Enhanced GaN decomposition in H_2 near atmospheric pressures

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GaN decomposition is studied at metallorganic vapor phase epitaxy pressures (i.e., 10–700 Torr) in flowing H_2. For temperatures ranging from 850 to 1050 °C, the GaN decomposition rate is accelerated when the H_2 pressure is increased above 100 Torr. The Ga desorption rate is found to be independent of pressure, and therefore, does not account for the enhanced GaN decomposition rate. Instead, the excess Ga from the decomposed GaN forms droplets on the surface which, for identical annealing conditions, increase in size as the pressure is increased. Possible connections between the enhanced GaN decomposition rate, the coarsening of the nucleation layer during the ramp to high temperature, and increased GaN grain size at high temperature are discussed. [S0003-6951(98)03540-2]

GaN has shown great promise for the production of blue light-emitting diodes,[1] lasers,[2] and for high-power electronic devices.[3] Improvements in the material quality have played a critical role in device performance breakthroughs.[1,2] The growth of high-quality GaN films on sapphire can be achieved using metallorganic vapor phase epitaxy (MOVPE) at temperatures above 1000 °C and V/III ratios larger than 1000. For MOVPE growth, the temperature is typically larger (i.e., 100–500 °C) than the threshold temperature for GaN decomposition.[4] The large V/III ratio is necessary to offset the N desorption rate at the growth temperature used for MOVPE growth,[5] however, the magnitude of GaN decomposition, which may occur during growth, is currently not well understood.

In a previous paper we have suggested that decomposition of the GaN film during growth may enhance GaN ordering, by eliminating weakly incorporated Ga and N atoms.[5] Growth conditions closer to equilibrium may be obtained when the incorporation and decomposition rates of atoms into the lattice are nearly equal with the incorporation rate being slightly larger than the decomposition rate for a positive growth rate.[5–7] In this letter, we focus on the GaN decomposition kinetics in flowing H_2. We show an enhancement in the GaN decomposition rate for pressures >100 Torr and describe how this enhanced decomposition may aid in improving the quality of GaN growth at these higher pressures.

GaN thermal decomposition has been extensively studied in vacuum.[4,8–12] From the previous studies, an activation energy E_A of 3.1 eV was measured for GaN decomposition.[9,10] This E_A is only slightly larger than the E_A of 2.8 eV for Ga desorption from liquid Ga,[13] suggesting a possible link between Ga desorption and GaN decomposition. These studies showed that GaN decomposes into metallic Ga atoms and N_2 molecules, which both desorb from the surface.[11] The formation and desorption of GaN clusters has also been observed.[12]

For this study, GaN films were grown on *a*-plane sapphire at 76 Torr using a close-spaced showerhead reactor design. After annealing the sapphire wafers in H_2 at 1080 °C, a thin ($\approx$200 Å) GaN nucleation layer was grown at 540 °C followed by ramping to 1020–1030 °C for growth of 2–3 μm of GaN. This growth process resulted in specular GaN growth, with excellent across wafer thickness uniformity. The temperature of the susceptor was calibrated by observing the melting point of 0.005 in. diam Au wire and correlating it to the setpoint of the heater measured with a thermocouple. The temperature calibration in the reactor was found to be reproducible to within 5 °C after eight months of use.

For the decomposition study, pieces of the GaN on sapphire were cleaved and weighed to within 0.1 mg using an analytical balance. The pieces were reintroduced into the reactor and heated under varying conditions using a 6.0 SLM flow of H_2. Each piece was ramped at 25 °C per minute to the annealing temperature. After annealing for a set time and cooling, each piece was reweighed in air to determine the mass loss. Repeated weighing of the same annealed pieces over time resulted in reproducible weights to within 0.1 mg, suggesting no net oxidation or water condensation of the annealed sample. When the pressure is 40 Torr or greater, liquid Ga droplets were observed. The liquid Ga droplets were found to be very stable in air. With the liquid Ga covered surface sitting in air for over a week, the Ga droplets could be coalesced into larger droplets by touching with a tweezer, proving the Ga droplets are liquid and not significantly oxidized. The Ga droplets were removed using dilute HNO_3 and rinsing with DI water. Each piece was weighed again. The weight of the GaN decomposed was calculated by subtracting the final weight from the initial weight. Likewise, the weight of the liquid Ga droplets was calculated by subtracting the final weight from the second weight. The weight of desorbed Ga was calculated from the mass balance difference between the decomposed GaN and the liquid Ga. Finally, the piece was annealed at 1080 °C to remove the remaining GaN. The weights were converted to kinetic rates (atoms/cm^2) by dividing by the sapphire area. The area of the

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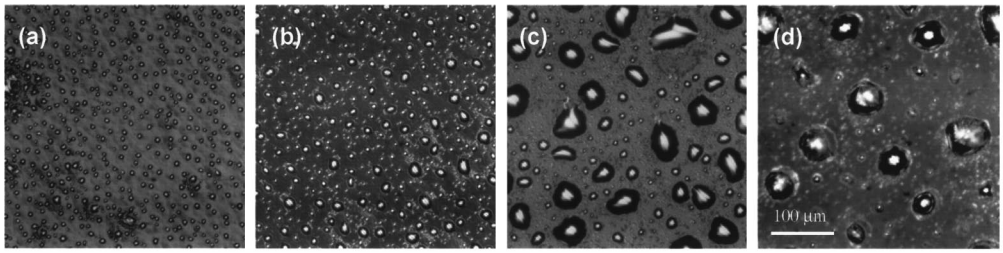

FIG. 1. Ga droplets on the GaN surface after annealing at 992 °C for 10 min at pressures of (a) 40 Torr, (b) 76 Torr, (c) 150 Torr, and (d) 700 Torr. Note the increase in size of the Ga droplets above 100 Torr. All images are the same scale with the bar on (d) indicating 100 μm.

irregularly shaped sapphire pieces was calculated using the formula $A=m/Td$, where m is the weight of the sapphire, T is the thickness of the sapphire wafer, which was typically 0.033 cm, and d is the sapphire density (3.98 g/cm^3).

The buildup of Ga droplets on the GaN surface is shown in Fig. 1 for a series of 10 min anneals at $T=992$ °C at pressures of (a) 40, (b) 76, (c) 150, and (d) 700 Torr. For pressures less than 40 Torr no Ga droplets were observed, which is consistent with previous vacuum experiments.[8–12] As shown in Fig. 1, there is a noticeable increase in the size of the largest Ga droplets as the pressure is increased from 76 to 150 Torr. The droplets are formed because the GaN decomposition rate exceeds the Ga desorption rate from the surface. The droplet size distribution suggests coalescence-dominated growth of the Ga droplets, similar to Ga droplet formation on GaAs when it is annealed above 600 °C.[14]

The surface Ga accumulation (droplet) rate, along with the GaN decomposition and Ga desorption rates are plotted in Fig. 2 as a function of pressure. Figure 2(a) shows the rates at 992 °C and Fig. 2(b) shows the rates at 901 °C. It is clear from Fig. 2(a) that the GaN decomposition rate (filled circles) increases as the pressure is increased. Furthermore, the surface Ga accumulation rate (open squares) increases as the pressure increases and appears to correlate with the increase in the GaN decomposition rate. The Ga desorption rate (filled diamonds) changes slightly as a function of pressure, peaking near 100 Torr. We speculate that this small increase is due to the liquid Ga surface area to volume ratio, which is maximized from 76 to 150 Torr and decreases as the size of the Ga droplets increase.

An Arrhenius plot of the Ga desorption rate k_{Ga} is shown in Fig. 3. The data for Fig. 3 were measured at 40, 76, 150, and 250 Torr. An exponential fit yields a preexponential of $(6.6\pm0.4)\times10^{29}$ cm^{-2} s^{-1} and an activation energy $E_{A,\mathrm{Ga}}$ of 2.74 ± 0.02 eV. This value for $E_{A,\mathrm{Ga}}$ is in excellent agreement with the value of 2.8 eV for Ga desorption from liquid Ga,[13] and 2.69 eV for Ga desorption from GaN in vacuum.[15] It appears that the Ga desorption rate is independent of H_2 pressure and depends solely on the liquid Ga surface area.

A more dramatic increase in the GaN decomposition rate is observed at a temperature of 901 °C as shown in Fig. 2(b). The annealing times for the data at 40 and 76 Torr were 45 and 60 min, while for the other pressures the annealing time was 10 min. As shown in Fig. 2(b), there is almost an order of magnitude increase in the GaN decomposition rate as the pressure is increased from 76 to 150 Torr. As in Fig. 2(a), the increase in the GaN decomposition rate correlates well with the increased Ga surface accumulation. A similar increase in the GaN decomposition rate is also observed at temperatures as low as 800 °C.

Currently, we do not understand the mechanism for the enhanced GaN decomposition as the pressure is increased. Clearly, from Fig. 2 the GaN decomposition rate coincides with the increase of liquid Ga on the surface, however, it is not clear if the Ga accumulation is the cause or a result of the enhanced decomposition. Ga metal is known to dissociate H_2 at high temperatures to form Ga hydrides,[16] which may be more mobile on the surface. This has been observed by Morishita and co-workers, who have shown that the Ga diffusion length is increased when H_2 or atomic H are used in the molecular beam epitaxy growth of GaAs.[17] In their interpretation of the increased Ga diffusion length, Morishita *et al.* speculated that the GaH_x species are more weakly bound to

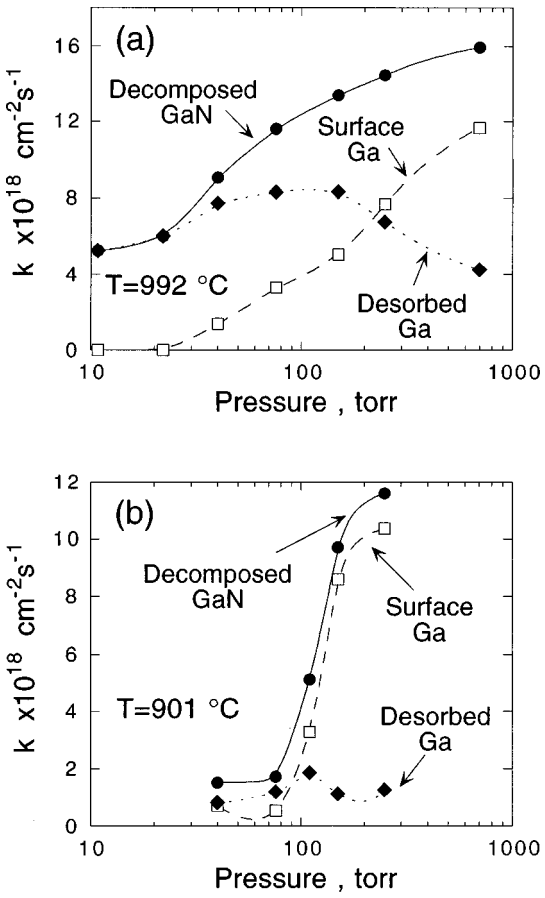

FIG. 2. Plot of the GaN decomposition rate (solid circles) at various pressures at (a) 992 °C and (b) 901 °C. The Ga desorption rate (solid diamonds) and the rate of Ga accumulation (open squares) on the surface during the anneal are also plotted.

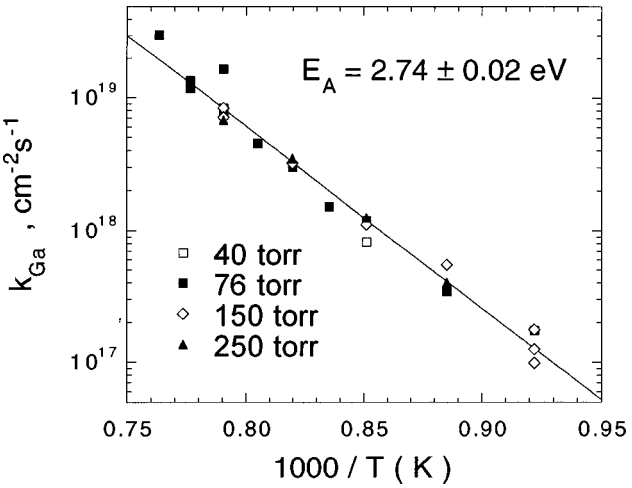

FIG. 3. Arrhenius plot of the Ga desorption rate measured at four different pressures versus the inverse temperature. All data are fit by $k_{\mathrm{Ga}}=(6.6\pm0.4)\times10^{29}\ \mathrm{cm}^{-2}\,\mathrm{s}^{-1}\ \exp(-2.74\pm0.02\ \mathrm{eV}/k_BT)$.

the surface, and therefore, can diffuse farther before incorporation.[17] The implication for the present study is that any increase in the Ga diffusion length would more rapidly uncover new areas of the GaN surface for N_2 desorption, which is 10–1000 times faster than the Ga desorption.[5,15] The active dissociation of surface H_2 may also occur on the highly polar GaN surface, and this may be enhanced at high pressures. Also, liquid Ga has recently been suggested to act as a catalyst to initiate and enhance GaN decomposition.[18] Further studies are underway to access the mechanism of the enhanced GaN decomposition.

One major impact of this study on the growth of GaN in our reactor is that the material quality is substantially improved when GaN growth is conducted above 100 Torr. When the GaN epitaxial layer is grown above 100 Torr, we find a near doubling of the mobility ($\mu>500\ \mathrm{cm}^2/\mathrm{V\,s}$ for intentionally Si-doped films with $n=2-3\times10^{17}\ \mathrm{cm}^{-3}$) compared to growth at 76 Torr. Other groups using close-spaced or high-speed rotating disk reactors have also reported improved electric properties when their GaN epitaxial growth is conducted above 100 Torr.[19,20] In the films grown above 100 Torr, the GaN grain size is increased to 2–5 μm compared to grain sizes of <1 μm for growth at 76 Torr. The reasons for the increased grain size are twofold and may be related to the enhanced GaN decomposition that occurs at higher pressures. It is known that during the temperature ramp from the nucleation layer to epitaxial growth conditions, the nucleation layer coalesces to form larger grains[21] with increased roughness.[22] If the ramp is conducted at high pressures, the nucleation layer grain may coalesce to a larger extent than at lower pressures. This increased coalescence is shown in the atomic force microscope data of Ref. 20 for a nucleation layer annealed at 100 Torr vs 140 Torr. In addition to increasing the nucleation layer coalescence, the enhanced GaN decomposition rate may aid in the ordering of the epitaxial film by increasing the decomposition and incorporation rates,[7] bringing the growth closer to equilibrium.[6] Studies are underway to determine the pressure influence on the coarsening of the nucleation layer before high-temperature growth. This study illustrates a possible major difference between reduced and atmospheric MOVPE GaN growth.

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[1] S. Nakamura, M. Senoh, and T. Mukai, Appl. Phys. Lett. **64**, 1687 (1994).
[2] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, Jpn. J. Appl. Phys., Part 2 **35**, L74 (1996).
[3] S. N. Mohammad, A. A. Salvador, and H. Morkoç, Proc. IEEE **83**, 1306 (1995); S. Strite and H. Morkoc, J. Vac. Sci. Technol. B **10**, 1237 (1992); R. F. Davis, Proc. IEEE **79**, 702 (1991).
[4] W. C. Johnson, J. B. Parsons, and M. C. Crew, J. Phys. Chem. **36**, 2651 (1932).
[5] D. D. Koleske, A. E. Wickenden, R. L. Henry, W. J. DeSisto, and R. J. Gorman, J. Appl. Phys. **84**, 1998 (1998).
[6] R. Heckingbottom, in *Molecular Beam Epitaxy and Heterostructures*, edited by L. L. Chang and K. Ploog (Martinus Nijhoff, Dordrecht, 1985), p. 71.
[7] S. Yu. Karpov and M. A. Maiorov, Surf. Sci. **393**, 108 (1997).
[8] R. J. Sime and J. L. Margrave, J. Phys. Chem. **60**, 810 (1956).
[9] Z. A. Munir and A. W. Searcy, J. Chem. Phys. **42**, 4223 (1965).
[10] R. Groh, G. Gerey, L. Bartha, and J. I. Pankove, Phys. Status Solidi A **26**, 353 (1974).
[11] R. C. Schoonmaker, A. Buhl, and J. Lemley, J. Phys. Chem. **69**, 3455 (1965).
[12] A. S. Bolgar, S. P. Gordienko, E. A. Ryklis, and V. V. Fesenko, in *Chemistry and Physics of the Nitrides*, edited by G. V. Samsonov [in Russian] (Naukova, Dumka, Kiev 1968), p. 151; also, see I. G. Pichugin and D. A. Yas'kov, Izv. Akad. Nauk SSSR, Neorg. Mater. **6**, 1973 (1970).
[13] R. E. Honig and D. A. Kramer, RCA Rev. **30**, 285 (1969).
[14] M. Zinke-Allmang, L. C. Feldman, and W. van Saarloos, Phys. Rev. Lett. **86**, 2358 (1992).
[15] O. Brandt, H. Yang, and K. H. Ploog, Phys. Rev. B **54**, 4432 (1996).
[16] H. Remy, *Treatise on Inorganic Chemistry* (Elsevier, New York, 1960), p. 18; W. R. S. Garton, Proc. Phys. Soc. London, Sect. A **64**, 509 (1951).
[17] Y. Morishita, Y. Nomura, S. Goto, and Y. Katayama, Appl. Phys. Lett. **67**, 2500 (1995).
[18] A. Pisch and R. Schmid-Fetzer, J. Cryst. Growth **187**, 329 (1998).
[19] B. T. McDermott, R. Pittman, E. R. Gertner, J. Krueger, C. Kisielowski, Z. Lilienthal-Weber, and E. Weber, Talk D2.2 at Fall Material Research Society Meeting, Boston, 1997.
[20] J. Han, T.-B. Ng, R. M. Biefeld, M. H. Crawford, and D. M. Follstaedt, Appl. Phys. Lett. **71**, 3114 (1997).
[21] A. E. Wickenden, D. K. Wickenden, and T. J. Kistenmacher, J. Appl. Phys. **75**, 5367 (1994).
[22] J. C. Ramer, K. Zheng, C. F. Kranenberg, M. Banas, and S. D. Hersee, Mater. Res. Soc. Symp. Proc. **395**, 225 (1996).